

PA 1054965  
F011L U 3 / 0 0 6 2 3  
23 SEP 2003

REC'D 06 OCT 2003  
WIPO PCT

PA 1054965

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 20, 2003

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM  
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK  
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT  
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/418,718

FILING DATE: October 17, 2002

PRIORITY DOCUMENT  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

BEST AVAILABLE COPY

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS

  
T. WALLACE  
Certifying Officer

A/PRW

Page 1 of 11129 U.S. PTO  
10/17/021129 U.S. PTO  
60/418718  
10/17U.S. PATENT AND TRADEMARK OFFICE  
PROVISIONAL APPLICATION FOR PATENT COVER SHEETThis is a request for filing a PROVISIONAL APPLICATION FOR PATENT  
under 37 C.F.R. §1.53(b)(2)

Atty. Docket: NATHAN 11

INVENTOR(S)/APPLICANT(S)			
LAST NAME	FIRST NAME	MI	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
NATHAN	Menachem		Tel Aviv, ISRAEL
PELED	Emanuel		Even Yehuda, ISRAEL
YUFIT	Vladimir		Ashdod, ISRAEL
<input type="checkbox"/> Additional inventors are being named on separately numbered sheets attached hereto			
TITLE OF THE INVENTION (280 characters max)			
THIN-FILM CATHODE FOR 3-DIMENSIONAL MICROBATTERY AND METHOD FOR PREPARING SUCH CATHODE			
CORRESPONDENCE ADDRESS			
Direct all correspondence to the address associated with Customer Number 001444, which is presently: BROWDY AND NEIMARK, P.L.L.C. 624 Ninth Street, N.W., Suite 300 Washington, D.C. 20001-5303			
ENCLOSED APPLICATION PARTS (check all that apply)			
<input checked="" type="checkbox"/> Specification	Number of Pages	17	<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 C.F.R. §1.27
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets	13	<input type="checkbox"/> Other (specify) _____
METHOD OF PAYMENT (check one)			
<input checked="" type="checkbox"/> Credit Card Payment Form PTO-2038 is enclosed to cover the Provisional filing fee of			
<input type="checkbox"/> \$160 large entity		<input checked="" type="checkbox"/> \$80 small entity	
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number 02-4035			

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

 No  Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

BROWDY AND NEIMARK, P.L.L.C.

By:

Sheridan Neimark  
Registration No.: 20,520Date: October 17, 2002  
SN:lb

**THIN-FILM CATHODE FOR 3-DIMENSIONAL  
MICROBATTERY AND METHOD FOR PREPARING SUCH  
CATHODE**

**FIELD OF THE INVENTION**

This invention relates in general to thin-film batteries. More specifically, the invention relates to a method for producing a cathode layer for thin-film microbatteries having a 3-D structure and the cathodes obtained by such method.

**LIST OF REFERENCES**

The following references are considered to be pertinent for the purpose of understanding the background of the present invention:

10 A. Albu-Yaron et al., Thin Solid Films 361-362 (2000) 223-228;  
Bates et al., U.S. Patent No. 5,338,625;  
Bates et al., U.S. Patent No. 5,567,210;  
Becker et.al., U.S. Patent 6,214,161;

15 J. J. Devadasan et al., Journal of Crystal Growth 226 (2001) 67-72;  
P. Fragnaud et al., Journal of Power Sources 54 (1995) 362-366;  
Laermer et al., U.S. Patents 5,498,312 and 6,303,512;

I. Martin-Litas et al., Journal of Power Sources 97-98 (2001), 545- 547;

20 Y. Miki et al., Journal of Power Sources 54 (1995) 508-510;  
Nathan et al., U.S. Patent No. 6,197,450;  
Norma R. de Tacconi et al., J. Phys. Chem. (1996), 100, 18234-18239;  
E. A. Ponomarev et al., Thin Solid Films 280 (1996) 86-89.

- 2 -

## BACKGROUND OF THE INVENTION

There is a global race to develop miniaturized power sources for applications including implantable medical devices, remote sensors, miniature transmitters, smart cards, and MEMS (micro-electro-mechanical-system) devices. Thin film lithium batteries are the leading candidates today, but the existing planar technology has limitations such as low energy density.

In thin-film battery technology the battery cell components can be prepared as thin, e.g. 1 micron, sheets built up in layers. The anode, the electrolyte and the cathode are in the form of thin films. Consequently, the anode is located close to the cathode resulting in high current density, high cell efficiency and reduction in the amount of reactants used.

The capacity of thin-film batteries is directly proportional to the area and thickness of the anode-electrolyte-cathode layers that form it. U.S. Patent No. 6,197,450 describes a method to increase the capacity of thin-film electrochemical devices by increasing the surface-to-volume ratio of the substrate upon which the layered thin-film structure is deposited. This is accomplished by etching the battery substrate to form an array of variable-shaped through-holes. The use of such a substrate increases the available area for thin film deposition, thus leading to an increase in volume, i.e. capacity of the cell. U.S. Patent No. 6,197,450 also describes a 3-dimensional (3-D) thin-film micro-battery with layers deposited inside the holes and on both flat surfaces of the substrate.

Several studies on cathode materials have been performed to improve the electrochemical performances of micro-batteries used in microelectronic devices. Some well-known materials used as the cathode (positive electrode) in lithium-ion batteries are  $\text{LiMn}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{LiCoO}_2$  and  $\text{TiS}_2$  which have been prepared in the form of a thin-film by various deposition methods.

U.S. Patents Nos. 5,338,625 and 5,567,210 disclose a novel vanadium oxide cathode and use of physical deposition techniques such as rf or dc

- 3 -

magnetron sputtering for the fabrication of thin-film lithium cells, especially thin-film micro-batteries having application as backup or primary integrated power sources for electronic devices. The batteries are assembled from solid-state materials, and can be fabricated directly onto a semiconductor chip, a chip 5 package or a chip carrier.

Others have disclosed methods of preparing different cathode materials. For example, P. Fragnaud et al. disclose a method of preparing a thin-film made of  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  for use as cathodes in secondary lithium batteries. These 10 films were prepared by chemical techniques such as CVD (chemical vapor deposition) and spray pyrolysis.

Also, I. Martin-Litas has disclosed the preparation of tungsten oxysulfide ( $\text{WO}_y\text{S}_2$ ) thin films by reactive radio-frequency magnetron sputtering.

Preparation of polycrystalline tungsten disulfide thin film by electrodeposition on conducting glass plates in galvanostatic route was described 15 by J. J. Devadasan et al. The obtained film was used for photoelectrochemical solar cells.

A  $\text{MoS}_2$  cathode material for lithium secondary batteries was synthesized by Y. Miki et al. by using thermal decomposition of  $(\text{NH}_4)_2\text{MoS}_4$  in a hydrogen gas flow at temperatures from 150 to 300°C.  $\text{MoS}_2$  thin films were also prepared by 20 electrochemical deposition by reduction of tetrathiomolybdate ions, as described by E. A. Ponomarev and A. Albu-Yaron. According to these publications  $\text{MoS}_2$  may be used for various applications such as solar cells, solid lubricants and rechargeable batteries.

A material which is useful in solar cells and in potentiometric sensor devices 25 is copper sulfide. Chemical sulfidisation of copper was described by N. R. de Tacconi et al, where the formation of copper sulfide films at copper anodes was accomplished in sulfide containing aqueous  $\text{NaOH}$  media.

Most of the known methods for the formation of thin films for battery 30 applications, including physical methods as sputtering and spray pyrolysis require flat surfaces and are therefore unsuitable for "conformal", three-dimensional (3-D)

- 4 -

structures in which the deposited films have to follow a surface's contour. Thus, present deposition methods are unacceptably disadvantageous for the production of 3-D thin film batteries.

### SUMMARY OF THE INVENTION

5 There is a need in the art to provide an inexpensive and relatively simple method for preparing cathode thin layers and may be carried out at ambient temperatures. The present invention provides a simple electrochemical method for the production of cathode active materials. The method of the invention enables to form thin film microbatteries, preferably 3-D microbatteries in ICP-etched 10 structures, or in any other substrates with through cavities of various shapes.

Thus, the present invention provides according to a first aspect thereof, a method for producing a thin film cathode comprising:

- 15 (i) electrolessly depositing a layer of a conducting material on the surface of a substrate, and
- 15 (ii) electrochemically depositing on the surface of said layer of conducting material a cathode active material which comprises sulfides or oxides of a transition metal and mixtures of such sulfides and oxides.

The layer of conducting material formed in step (a) serves as current 20 collector and is made of a metal compatible with the cathode active material such as Cu, Ni, Co, Fe, Au, Ag, Pd, Pt or their alloys. The cathode active materials formed in step (b) are selected from  $\text{Cu}_2\text{S}$ ,  $\text{MoS}_2$ ,  $\text{Co}_x\text{S}_y$ ,  $\text{Fe}_x\text{S}_y$  where  $x = 1-4$  and  $y=1-10$ ,  $\text{Co}_m\text{O}_n$ ,  $\text{Mo}_m\text{O}_n$  where  $m=1-2$ , and  $n=1-3$ ,  $\text{WS}_2$ , and mixtures thereof.

The cathode prepared by the method of the invention may be used in high 25 energy-density micro-electrochemical energy storage devices such as Li or Li ion microbatteries. According to a preferred embodiment, the insulating substrate is provided with a plurality of through cavities of arbitrary shape, for example a cylindrical shape. The cavities are characterized by having an aspect ratio greater than 1, more preferably between 2 to about 50. The microbattery components are

deposited between the cavities and throughout the inner surface of the cavities.

The insulating or semiconducting substrate may be made from glass, alumina, semiconducting materials, ceramic materials, organic polymers, glass-epoxy composites silicon or silicon-containing materials and the like. The 5 thin film cathode layer prepared by the method of the invention provides another aspect of the present invention. The thin film cathode film is formed on a substrate which is made of an insulating, semiconducting or electronically conducting material and is preferably provided with a plurality of through cavities of arbitrary shape, having an aspect ratio greater than 1.

#### 10 BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 is a SEM of through cavities in the form of cylindrical holes; A- top view;  
15 B- cross section.

Fig. 2 is a schematic presentation of a 3-D, thin film battery on-chip.

Fig. 3 - SEM of a Cu<sub>2</sub>S layer on a flat, silicon substrate coated with a Cu layer.

Fig. 4- XRD of Cu<sub>2</sub>S on silicon substrate coated with a Cu layer.

Fig. 5 -Charge-discharge curves of Li/CPE/Cu<sub>2</sub>S microbattery at 120°C.

20 Fig. 6 -Capacity loss of Li/CPE/Cu<sub>2</sub>S microbattery.

Fig. 7- SEM of MoS<sub>2</sub> on silicon substrate covered with a Ni layer.

Fig. 8 -Charge-discharge curves of Li/HPE/MoS<sub>2</sub> microbattery at room temperature.

Fig. 9 - Capacity loss of Li/HPE/ MoS<sub>2</sub> microbattery.

25 Fig. 10-Capacity loss of Li-ion/HPE/MoS<sub>2</sub> microbattery.

Fig. 11- Charge-discharge curve of Li/CPE/MoS<sub>2</sub> microbattery at 120°C.

Fig. 12-Capacity loss of Li/CPE/ MoS<sub>2</sub> microbattery

Fig. 13-Charge/discharge curves of Li-ion/HPE/CoS microbattery.

## DETAILED DESCRIPTION OF THE INVENTION

Battery capacity is directly proportional to the area and thickness of the thin film (anode-electrolyte-cathode) layers, which form it. An increase in the surface-to-volume ratio of the substrate upon which the layered thin-film structure is deposited may be achieved by, for example, etching the substrate (say silicon) to form an array of through-holes (cavities) of various shapes, by various dry etching techniques. New etching technologies, such as the Inductive Coupled Plasma (ICP) Bosch process (see US Patents 5,498,312 and 6,303,512 to 5 Laermer, and 6,214,161 to Becker et.al.) can etch structures with very high aspect (height-to-width) ratios, for example holes with a diameter of between 4 to 10 200  $\mu\text{m}$ , through a Si substrate having a thickness of between 20 to 500  $\mu\text{m}$ . If battery tri-layer film structures can be deposited conformally (i.e. following the contour of the substrate) into these holes, providing continuity from one side of 15 the substrate to the other, a 3-D structure is formed, and the film area (and volume) and consequently the battery capacity per unit volume of the substrate is increased significantly. For example, for a hole with diameter  $d$  in a wafer of thickness  $h$  (aspect ratio =  $h/d$ ), the ratio  $k$  of surface area after etching to the original, "planar" state is  $2h/d$ . For a square cavity with side  $a$  in the same wafer, 20  $k=2h/a$ . Thus, for a typical wafer with  $h = 400\mu\text{m}$  and  $d = 15\mu\text{m}$ , the increase in area is  $k=53$ , while for  $d=10\mu\text{m}$ ,  $k=80$ . This means a theoretical increase in capacity to about 10,000  $\mu\text{Ah}$  per 1  $\text{cm}^2$ .

For complete assembling of a microbattery, a few layers must be deposited sequentially and conformally on the silicon substrate: current collectors, 25 electroactive materials (cathode and anode) and an ion-conductive separator.

### A. Substrate preparation

A silicon substrate containing arrays of through-holes was prepared using photolithography and deep reactive ion etching (DRIE). The 3" silicon wafer was

- 7 -

double polished, (100) orientation, with a thickness of about 440  $\mu\text{m}$ . The wafer was coated on one side with about 11  $\mu\text{m}$  of AZ-4562 photoresist, and arrays of square holes with a side dimension of 80  $\mu\text{m}$  and inter-hole spacing of about 220  $\mu\text{m}$  were defined. The sequence of photolithography steps includes:

5

1. Dehydration bake of wafers after cleaning - 2min. at the temperature 110°C on a hot plate;

2. Dispensing photoresist and spinning at about 1400 RPM for 30 seconds,

10 3. Solvent removal bake at 110°C for 1 min. on a hot plate,

4. Exposure for between 17 to 22 seconds in a mask aligner,

5. Developing for 4-6 minutes in AZ-726 developer, and

6. Hard bake at 110°C for 3 minutes on the hot plate;

15

After photolithography, holes were etched using DRIE in a Plasma -Therm SLR 770 ICP system using a standard Bosch process.

Fig. 1A shows the SEM micrograph of a perforated silicon substrate, from top view, while Fig. 1B shows the SEM micrograph of the cross section of same substrate. As can be seen from the image, through cylindrical channels of about 20 40mm diameter are obtained by the ICP etching method.

### B. Deposition of layers

There are two optional configurations of the high surface area, 5 3-dimensional "on-chip" microbattery (3D-MB). The first one (3D-MB-1), in which the cathode material is deposited directly onto the silicon surface, and the second (3D-MB-2), as described in U.S. Patent No. 6,197,450, incorporated herein by reference, where the anode material (lithium or carbon) is in electronic contact with the substrate. In the latter case an additional layer between Si and C 10 or Li must be created in order to eliminate intercalation of Li-ions into the bulk of silicon at low voltage. Fig. 2 shows the 3D-MB-2 concept.

One example for a thin film cathode deposited according to the method of the present invention is that of copper sulfide. The silicon substrate was pretreated 15 in solutions of  $H_2O$  (5): $H_2O_2$ (1): $NH_4OH$ (1),  $H_2O$  (6): $H_2O_2$ (1): $HCl$ (1) at  $T= 80 - 100$  °C and in isopropanol, for removing oxides and organic contaminations. The sample was further wet-etched in a strong basic solution, rinsed in water and immediately immersed in a Pd-containing solution for increasing of catalytic 20 activity of the silicon substrate surface. Electroless deposition of copper on the silicon substrates was carried out in a  $CuSO_4/HCOH$  solution and resulted in a uniform copper thin film of 500-700 nm. Copper-deposited silicon samples were immersed into an electrolyte solution containing  $Cu^{2+}$  ions and surfactant materials. Electrochemical copper deposition was carried out at constant current 25 density (20-50 mA/cm<sup>2</sup>) for a few minutes. A thicker layer (5-20 micron) of copper was formed on these silicon samples. This layer serves as the current collector layer. Copper-deposited silicon substrates were introduced at room temperature into an aqueous solution of polysulfides (mixture of 10mM  $Na_2S$ , 0.1M  $NaOH$  and elemental sulfur) and electrooxidized at a constant current of 0.1 30 mA/cm<sup>2</sup>-0.5 mA/cm<sup>2</sup> for a few seconds. As a result, a thin (1-3 micron) cathode layer of crystalline (verified by XRD)  $Cu_2S$  was formed on the copper-coated

- 9 -

silicon. The copper electrode was cathodically polarized prior to  $\text{Cu}_2\text{S}$  film growth to reduce any residual oxide layer.

Fig. 3 shows the SEM cross-sectional view of the copper sulfide layer deposited onto copper coated silicon wafer. The crack between Cu and  $\text{Cu}_2\text{S}$  layers, seen in the lower part of this image, is caused by quenching in liquid nitrogen, which was used for cross-section cutting of the cathode.

The powder XRD analysis of the as-deposited films (Fig.4) on silicon revealed crystallographic peaks belonging to the deposited Cu layer and  $\text{Cu}_2\text{S}$ . Charge/discharge curves of the  $\text{Cu}_2\text{S}$ /composite polymer electrolyte/lithium battery operating at 120°C and current density of 50mA/cm<sup>2</sup> is represented by with well-pronounced plateau at about 2.1V (Fig.5). The capacity loss of the battery is about 1.4%/cycle, as showed in Fig.6.

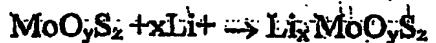
Another example of a cathode formed using the method of the present invention includes a thin film cathode of  $\text{MoS}_2$  obtained by cathodic reduction. A silicon substrate, electrolessly coated with a thin film of nickel (having a thickness of 200-300 nm) which serves as the current collector layer, was immersed into a solution containing  $\text{MoS}_4^{2-}$  ions. The formation of an ultra thin film (300-600 nm) of  $\text{MoS}_2$  was accomplished by electroreduction of  $\text{MoS}_4^{2-}$  ions on nickel-coated silicon samples at a constant current density of 10-15 mA/cm<sup>2</sup>.

Fig. 7 shows a SEM micrograph of the cross-section of a cathode deposited on a nickel-coated silicon substrate. A compact, highly adherent film of about 300 to 600 nm-thick is built. The powder XRD analysis of the as-deposited film on nickel revealed crystallographic peaks belonging to the nickel substrate alone. This may indicate the formation of mainly amorphous  $\text{MoS}_2$  deposits.

25

The next step in the formation of a microbattery according to the present invention is the deposition of an ion conductive electrolyte on the already-deposited cathode layer. This was achieved by casting a soluble polymer mixture directly onto the cathode. Two types of conductive separators have been used. The first is a composite polymer electrolyte based on poly(ethylene oxide),

a lithium salt such as lithium iodide, lithium trifluoromethanesulfonate, lithium trifluoromethanesulfonimide, lithium bis-oxaloborate, etc. and alumina or silica nanoparticles. The second type is a so called hybrid gel-polymer electrolyte (HPE) based on a nanoporous membrane of poly(vinylidene flouride) soaked with a lithium salt ( $\text{LiPF}_6$  or Li-Imide) dissolved in the EC:DEC (ethylene carbonate : diethylcarbonate) electrolyte. Solvents, such as: diglyme (DG), tetraglyme (TG), polyethylene glycol dimethyl ether (PEGDME, MW 500) can be used in HPEs as well. Fig. 8 shows typical charge-discharge curves of  $\text{Li}/\text{HPE}/\text{MoO}_y\text{S}_2$  cell, with the cathode deposited on a nickel substrate. The cell was cycled at room temperature and  $i_d = i_{ch} = 10 \mu\text{A}/\text{cm}^2$ . The sloping character of the curves is typical to insertion/de-insertion process into a single-phase host material according to the following reaction:



It is to be emphasized that up to ten-fold increase in the current density did not influence both the shape of the curves (curve b, in comparison to curve a), and the degradation rate. About 0.8 and 0.6 mole atoms of lithium was reversibly intercalated at low and high current density, respectively. The 1<sup>st</sup> cycle utilization of the cathode active material approached 85%. The Li/HPE/MoO<sub>2</sub>S<sub>2</sub> cell ran over 1000 successive cycles with 0.05%/cycle capacity loss and 100% Faradaic efficiency, as showed in Fig. 9. Fig. 10 shows the plots of capacity loss and charging efficiency of the Li-ion/HPE/ MoS<sub>2</sub> cell with the cathode deposited on nickel coated silicon substrate. The cell was cycled at room temperature and 100  $\mu$ A/cm<sup>2</sup> rate. As can be seen from the Fig. 10, similarly to the previous case, during more than 1000 reversible 100%DOD cycles the degradation rate did not exceed 0.05%/cycle and the Faradaic efficiency was close to 100%. Charge/discharge of Li/LiImide;P(EO)<sub>20</sub>EC; 12% (v/v) Al<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> cell was carried out at 125°C (Fig.11). While the same charge-discharge mechanism has been expected in this electrochemical system, the degradation degree in Li/CPE/MoS<sub>2</sub> cell was higher than in HPE-consisting battery: 0.5%/cycle (Fig.12). This may be caused by poor contacts and insufficient ionic mobility in

the all-solid-state battery. Noteworthy, that no self-discharge was detected in all the Li/MoS<sub>2</sub> cells under investigation. Slow overdischarge to 0.2V does not affect the subsequent cycling behavior of the Li/MoS<sub>2</sub> batteries.

In order to improve the performance characteristics of a battery, it is known in the art to form a protective layer on cathodes. Such modification involves the coating of pyrite particles by a very thin ion-conductive protective film, known as the solid electrolyte interphase (SEI). The formation of SEI on cathodes provides protection to the cathode active material in fully charged and/or fully discharged states and improves the performance characteristics of the battery. For high performance characteristics of lithium and Li-ion battery the SEI must be the electronic resistor and ionic conductor. A novel use of this technique is described in the present invention, according to which a SEI is built in situ as a solid ion-conducting electrolyte in 3D-microbatteries. The SEI is electrochemically formed by overdischarge of the cell during 1<sup>st</sup> and possibly few following cycles. This procedure may be carried out during electrochemical lithiation of graphite in Li-ion batteries

For a lithium battery, a metallic lithium electrode was used as anode material. For lithium-ion applications, additional casting of lithiated graphite particles with polymer used as a binder is needed. Alternatively, there is a possibility to make a microbattery in a slightly different way, when the layer deposited on the current collector is the anode and not the cathode. This can be done by electrochemical deposition of an anode material such as Sn<sub>x</sub>Sb<sub>y</sub> onto the first layer of current collector, or by chemical vapor deposition of a carbonaceous precursor on nickel -deposited silicon (a nickel coating would act also as a catalyst), with successive formation of a soft carbon that can be used further as an anode for lithium-ion batteries.

For the three-dimensional batteries of both 3D-MB-1 structure, (in which the cathode material is deposited directly onto the substrate surface), and the 3D-MB-2 structure (where the anode material is in electronic contact with the substrate) the filling of cylindrical holes of the perforated silicon by HPE and

- 12 -

lithiated graphite can be performed by spinning and/or vacuum.

### Microbattery Performance

5 Examples of the performance of microbatteries involving these electrochemically deposited cathodes include that of a planar thin film Li/copper sulfide-on silicon battery cycled with solid polymer and gel electrolyte at 120°C and at room temperature. The degree of degradation of both cells was in the range of 1.5-2.5 %/cycle. The capacity loss of a Li/solid polymer electrolyte/mixed 10 cobalt cathode cell was about 3%/cycle. Another example includes a planar 1cm<sup>2</sup> Li/gel polymer electrolyte/molibdenum sulfide cell that went through over 1000 reversible cycles with a capacity loss of less than 0.1%/cycle at room temperature. 3D Li-ion/HPE/MoS<sub>2</sub> battery went over 50 reversible cycles with capacity loss about 0.5%/cycle.

15 Microbatteries routinely go more than 100 cycles. The thin-film Cu<sub>2</sub>S/Li battery can operate both at room temperature and at moderate temperature 120°C. The cell delivers a rechargeable capacity of 160 mAh/g with a flat potential plateau at ca. 1.6V vs. Li/Li<sup>+</sup>.

## 20 EXAMPLES

### Example 1

25 A secondary electrochemical cell, consisting of a lithium anode, hybrid polymer electrolyte and MoS<sub>2</sub> cathode on silicon substrate was assembled.

In order to remove organic and metallic residues, the silicon substrate was immersed into mixture solution of H<sub>2</sub>O<sub>2</sub>: NH<sub>4</sub>OH for 5 min at 70 C and washed in deionized water with successive immersion into H<sub>2</sub>O<sub>2</sub>: HCl mixture for another 5 min. After rinsing in deionized water the substrate was etched in NH<sub>4</sub>F: HF

solution for 2 min. The surface activation was accomplished in  $\text{PdCl}_2\text{:HCl:HF:CH}_3\text{COOH}$  solution at room temperature for 2 min.

A  $0.3\text{ }\mu\text{m}$  thick cathode was prepared by reduction of  $\text{MoS}_4^{2-}$  ions on nickel coated silicon substrate at constant current density of  $10\text{-}15\text{ mA/cm}^2$ . Nickel deposition was carried out in  $\text{NiSO}_4\text{:NaH}_2\text{PO}_2\text{:EDTA}$  (or  $\text{CH}_3\text{COONa}$ ) solution with  $\text{pH}=4$  and at elevated temperature (90 deg. C) for a few minutes. The thickness of deposit is a function of time and can be varied.

Deposition of  $\text{MoS}_2$  was carried out from aqueous solution of 0.05M tetrathiomolybdate. Potassium chloride (0.1 M) was the supporting electrolyte. Electrodeposition was carried out at room temperature. The electrodeposition was accomplished under constant current density of  $10\text{ mA/cm}^2$  for 4 min. The deposited samples were thoroughly rinsed in deionized water and vacuum-dried at elevated temperature.

SEM micrographs (Fig. 1) reveal that the films deposited at room temperature are fairly continuous without visible cracks. EDS measurements showed 1:2 Mo:S ratio. XPS data supported this composition. The films were X-ray transparent, indicating amorphous structure of  $\text{MoS}_2$ .

The chosen polymer for hybrid polymer electrolyte (HPE) is commercially available PVDF-2801 copolymer (Kynar). The PVDF powder was dissolved in high-purity cyclopentanone (Aldrich). Fumed silica 130 (Degussa) and propylene carbonate (PC, Merck), similar to the Bellcore process, were added and the mixture was stirred at room temperature for about 24 hours to get homogeneous slurry. After complete dissolution, the slurry was cast on the Teflon support and spread with the use of the doctor-blade technique. To prevent surface irregularities, the film was then covered with a box pierced with holes that allowed a slow evaporation of the cyclopentanone. After complete evaporation of the cyclopentanone, a 13mm diameter disc was cut from the polymer membrane. It was soaked in Liimide-based electrolyte for 48 hours. In order to ensure a complete exchange of the PC by electrolyte, at least three fresh portions of electrolyte were

- 14 -

used for each soaking. Liimide-ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1 (v/v) based electrolytes were stored in a glove box with Li chips.

The Li/HPE/MoS<sub>2</sub> cells were cycled at room temperature using a Maccor series 2000 battery test system. The voltage cut-off was 1.3 to 2.4 V. 5 charge/discharge current density – 10-100  $\mu$ A/cm<sup>2</sup>. The Li/HPE/MoS<sub>2</sub> cell delivered above 20  $\mu$ Ah per cycle at 100  $\mu$ A/cm<sup>2</sup> (Fig. 9) for over 1000 reversible cycles with the capacity fade of 0.05 %/cycle. The Faradaic efficiency was close to 100%.

### Example 2

10 A Li/composite polymer electrolyte (CPE)/MoS<sub>2</sub> battery was assembled. The cathode was prepared as in Example 1.

15 A 50  $\mu$ m thick film composite polymer electrolyte with a composition of Liimide, P(EO)<sub>20</sub> EC, 9% v/v Al<sub>2</sub>O<sub>3</sub> was prepared from 45 mg Liimide, 300 mg P(EO), 30 mg EC and 100 mg Al<sub>2</sub>O<sub>3</sub>.

15 Poly(ethylene oxide) (P(EO)) was purchased from Aldrich, (average molecular weight  $5 \times 10^6$ ) and was vacuum dried at 45 to 50 °C for about 24 hours. A polymer slurry was prepared by dispersing known quantities of P(EO), Liimide, and ethylene carbonate (EC) in analytical grade acetonitrile, together with the 20 required amount of an inorganic filler, such as Al<sub>2</sub>O<sub>3</sub> (Buehler) with an average diameter of about 150A. To ensure the formation of a homogeneous suspension, an ultrasonic bath or high-speed homogenizer was used. The suspension was stirred for about 24 hours before the PE films were cast on the fine polished Teflon support (64 cm<sup>2</sup> area). The solvent was allowed to evaporate slowly and then the 25 films were vacuum dried at 120 °C for at least 5 hours. The final thickness of the solvent-free PE films was between 30 to 50  $\mu$ m thick.

The Li/composite polymer electrolyte (CPE)/MoS<sub>2</sub> battery was cycled at 120°C and current density 50 mA/cm<sup>2</sup>. The voltage cutoff on discharge was 1.1 V. The voltage cutoff on charge was 2.2 V (Fig.11). The cell went through over 40

- 15 -

reversible cycles (100% DOD), and the degree of degradation did not exceed 0.5 %/cycle. (Fig. 12).

### 5 Example 3

A Li/CPE/Cu<sub>2</sub>S cell with a 1  $\mu$ m thick film composite cathode was prepared and assembled as described in Example 1, starting with the following starting materials: 33 mg LiI, 216 mg P(EO), 41 mg EC, 100mg Al<sub>2</sub>O<sub>3</sub>. 100% Dense Cu<sub>2</sub>S cathode was prepared by anodic oxidation of metallic copper layer electrodeposited 10 on the electroless copper. The silicon substrate was pretreated in solutions of H<sub>2</sub>O (5):H<sub>2</sub>O<sub>2</sub>(1):NH<sub>4</sub>OH(1), H<sub>2</sub>O (6):H<sub>2</sub>O<sub>2</sub>(1):HCl(1) at T= 80 –100 °C and in isopropanol, for removing oxides and organic contaminations. The sample was further wet-etched in a strong basic solution; rinsed in water and immediately 15 immersed in a Pd-containing solution for increasing of catalytic activity of the silicon substrate surface. The solution for electroless copper deposition consisted of (g/L): 10-15 CuSO<sub>4</sub>·5H<sub>2</sub>O, 10-15 NaOH, 2-3 NiCl<sub>2</sub>·H<sub>2</sub>O, 0.001 Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 15-25mL/L HCOH (37%)

The electrolyte for copper electrodeposition contained (g/L): 200-250 CuSO<sub>4</sub>·5H<sub>2</sub>O and 50-60 H<sub>2</sub>SO<sub>4</sub>. The electrodeposition was performed at room 20 temperature and current density of 50 mA/cm<sup>2</sup> for 8 min. This copper layer was electrooxidised in an aqueous solution of polysulfides (mixture of 10mM Na<sub>2</sub>S, 0.1M NaOH and elemental sulfur) at a constant current of 0.1 mA/cm<sup>2</sup>-0.5 mA/cm<sup>2</sup> for a few seconds. SEM micrograph of the silicon-copper-copper sulfide layers is shown in Fig. 3. XRD data affirm the obtaining of Cu<sub>2</sub>S compound (Fig.4).

25 The Li/CPE/Cu<sub>2</sub>S cell went through over 50 reversible cycles, and the degree of degradation did not exceed 1.5 %/cycle. (Figs. 5, 6).

**Example 4**

1 A Li/HPE/Cu<sub>2</sub>S cell with a 1  $\mu\text{m}$  thick film cathode was prepared and  
assembled as described in Examples 2 and 3. The cell went through over reversible  
5 120 cycles (100% DOD), with the degree of degradation being 0.8 %/cycle.

**Example 5**

10 A Li/CPE/WS<sub>2</sub> cell with a 0.4  $\mu\text{m}$  thick film composite cathode was  
prepared as described in Example 2. The cell went through over 135 reversible  
cycles (100% DOD), and the degree of degradation did not exceed 0.2 %/cycle

**Example 6**

15 A Li/CPE/Cu<sub>2</sub>S cell with a 2  $\mu\text{m}$  thick film composite cathode with a Li<sub>2</sub>S<sub>6</sub>  
to LiI ratio = 1 : 0.25 was assembled as described in Example 3. The Li/CPE/ Cu<sub>2</sub>S  
cell was cycled for over 40 (100% DOD) cycles.

**Example 7**

20 A Li/CPE/Co<sub>x</sub>Sy cell with a 0.3  $\mu\text{m}$  thick film composite cathode with a  
was assembled as described in Example 3. 100% dense Co<sub>x</sub>Sy cathode was  
prepared by electrochemical oxidation of metallic Co in the solution of  
polysulfides. The Li/CPE/ Co<sub>x</sub>Sy cell was cycled for over 30 (100% DOD) cycles  
(Fig. 13).

25

**Example 8**

30 A lithium-ion/MoS<sub>2</sub> cell with a 0.5  $\mu\text{m}$  thick film cathode and hybrid  
polymer electrolyte was prepared according to the procedure of Example 1. The  
HPE casting was performed onto cathode deposited silicon. The lithiation of  
graphite powder was carried out as follows:

- 17 -

1. Polymer binder (polystyrene) was dissolved in toluene. After dissolution, graphite powder (of few  $\mu$ micron?m average particle size) was added to the mixture. The resulted slurry was spread on copper current collector by doctor blade. 2. This electrode was vacuum dried and assembled with lithium and ion-conductive separator (Celgard soaked in 1M LiPF<sub>6</sub> EC:DEC 1:1 v/v) in cells. 3. After few successive cycles, the cells were disassembled and lithiated electrode was rinsed in DMC and vacuum dried.

The lithiated graphite electrodes were used as anodes in Li-ion/HPE/MoS<sub>2</sub> on- silicon battery. The battery was reversibly charged-discharged for over than 1000 cycles with capacity loss of 0.06%/cycle. The Faradaic efficiency was close to 100 %. The battery delivered about 10  $\mu$ Ah per cycle (Fig.10).

#### Example 9

A 3D-lithium-ion/MoS<sub>2</sub> cell with a 0.3  $\mu$ m thick film cathode and hybrid polymer electrolyte was prepared according to the procedure of Examples 1 and 8. The electrodeposition was carried out in 0.05M tetrathiomolybdate electrolyte. Lithiated graphite (see Example 8) was pilled off from the copper electrode and introduced into toluene solution. Few hours of stirring resulted in homogenous mixture of lithiated graphite and binder in toluene. The filling of cylindrical holes of the perforated silicon by HPE and lithiated graphite was performed by spinning. The battery was reversibly charged-discharged for 50 cycles and delivered 35  $\mu$ Ah per cycle. The Faradaic efficiency was close to 100 %.

**CLAIMS:**

1. A method for producing a thin film cathode comprising:
  - (a) electrolessly depositing a layer of a conducting material on the surface of a substrate, and
  - 5 (b) electrochemically forming on the surface of said layer of conducting material a cathode material which comprises sulfides or oxides of a transition metal and mixtures of such sulfides and oxides.
2. A method according to claim 1, said cathode being used in a high energy-density micro-electrochemical energy storage cell.
- 10 3. A method according to claim 2, wherein said micro-electrochemical energy storage cell is a Li or Li ion microbattery.
4. A method according to claim 1 wherein said substrate is provided with a plurality of through cavities of arbitrary shape, having an aspect ratio greater than 1 and said cathode material is deposited between said cavities and throughout the 15 inner surface of said cavities.
5. A method according to claim 4, wherein the through cavities of the substrate have an aspect ratio of between 2 to about 50.
6. A method according to claim 4, wherein said cavities have a cylindrical geometry.
- 20 7. A method according to Claim 1 wherein said substrate is selected from the group consisting from glass, alumina, semiconductor materials, ceramic materials, organic polymers, inorganic polymers and glass-epoxy composites.
8. A method according to Claim 7, wherein said semiconductor material is silicon.
- 25 9. A method according to Claim 1, wherein said layer of conducting material formed in step (a) is compatible with the cathode active material, and selected from Cu, Ni, Co, Fe, Au, Ag, Pd, Pt and their alloys
10. A method according to Claim 1, wherein said cathode materials are selected from Cu<sub>2</sub>S, MoS<sub>2</sub>, Co<sub>x</sub>S<sub>y</sub> where x = 1-4 and y=1-10, Co<sub>m</sub>O<sub>n</sub> where m=1-2 and

- 19 -

$n=1-3$ ,  $WS_2$ , and mixtures thereof.

11. A thin film cathode layer being prepared by the method of claim 1.

12. A thin film cathode layer being prepared by the method of Claim 1 on a substrate provided with a plurality of through cavities of arbitrary shape, having an aspect ratio greater than 1 and said cathode layer being deposited between said cavities and throughout the inner surface of said cavities.

13. A microbattery comprising the cathode of claim 11.

14. A self-powered semiconductor component comprising a microbattery according to claim 13.

10

15

20

25

- 20 -

### ABSTRACT

The present invention provides a method for producing a thin film cathode. The method comprises the steps of electrolessly depositing a layer of a conducting material on the surface of a substrate, and electrochemically depositing on the surface of said layer of conducting material a cathode active material which comprises sulfides or oxides of a transition metal and mixtures of such sulfides and oxides. The cathode prepared by the method of the invention may be used in high energy-density micro-electrochemical energy storage devices such as Li or Li ion microbatteries. According to a preferred embodiment, the insulating substrate is provided with a plurality of through cavities of arbitrary shape, for example a cylindrical shape.

2014-10-18 10:17:02

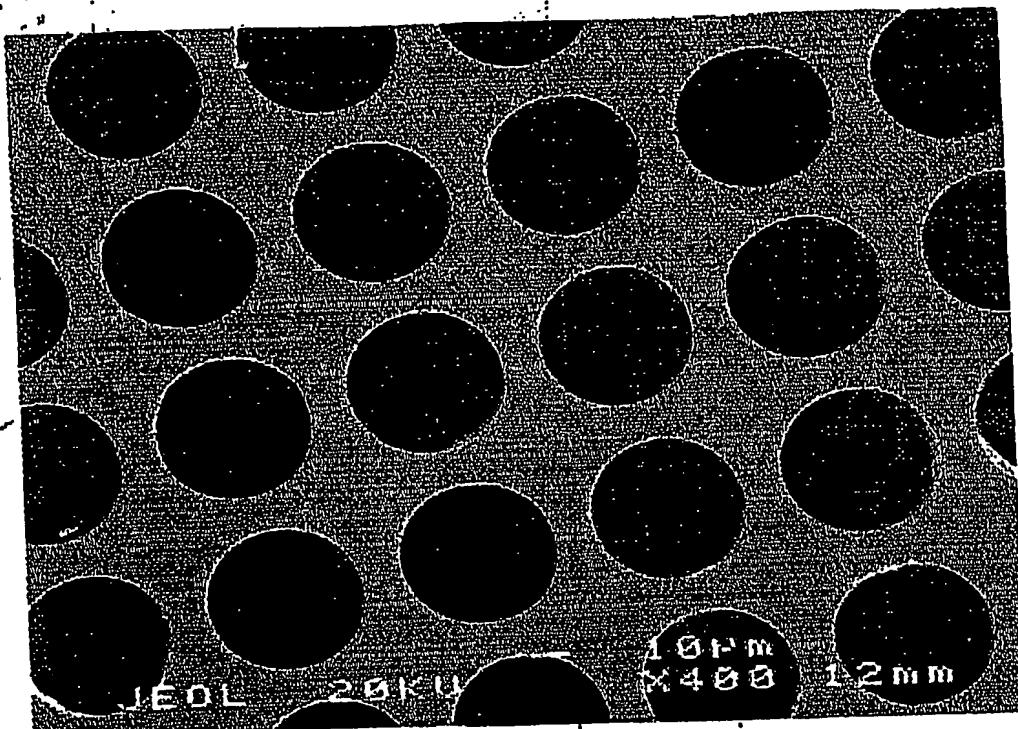


Fig. 1A

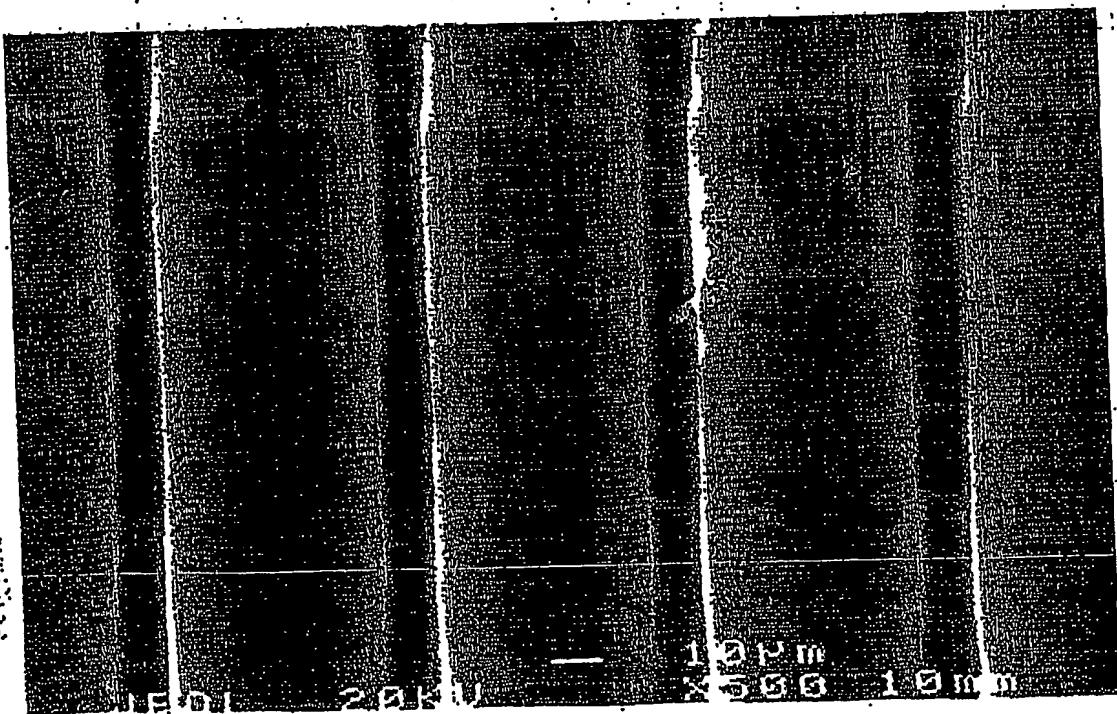


Fig. 1B

## 3D-Microbattery concept

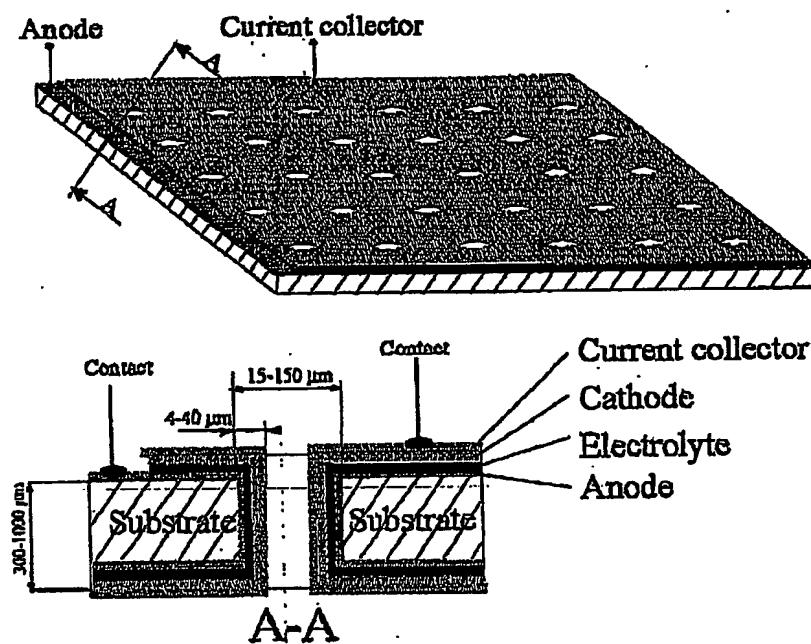


Fig.2

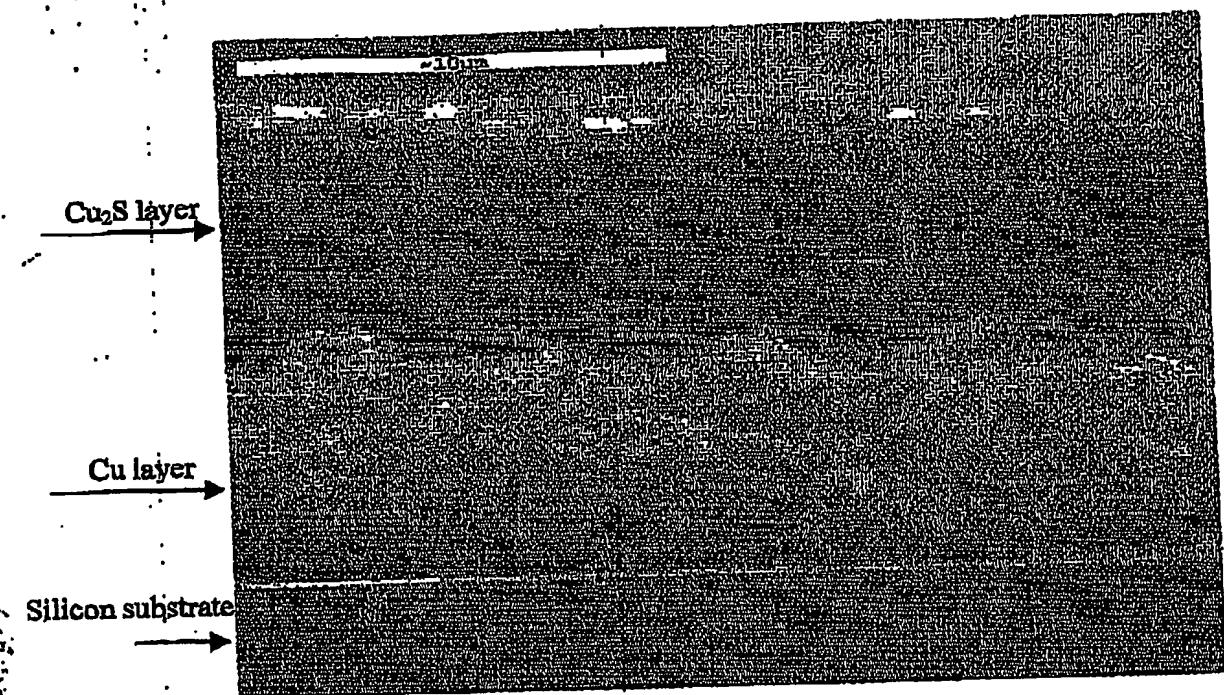


Fig. 3

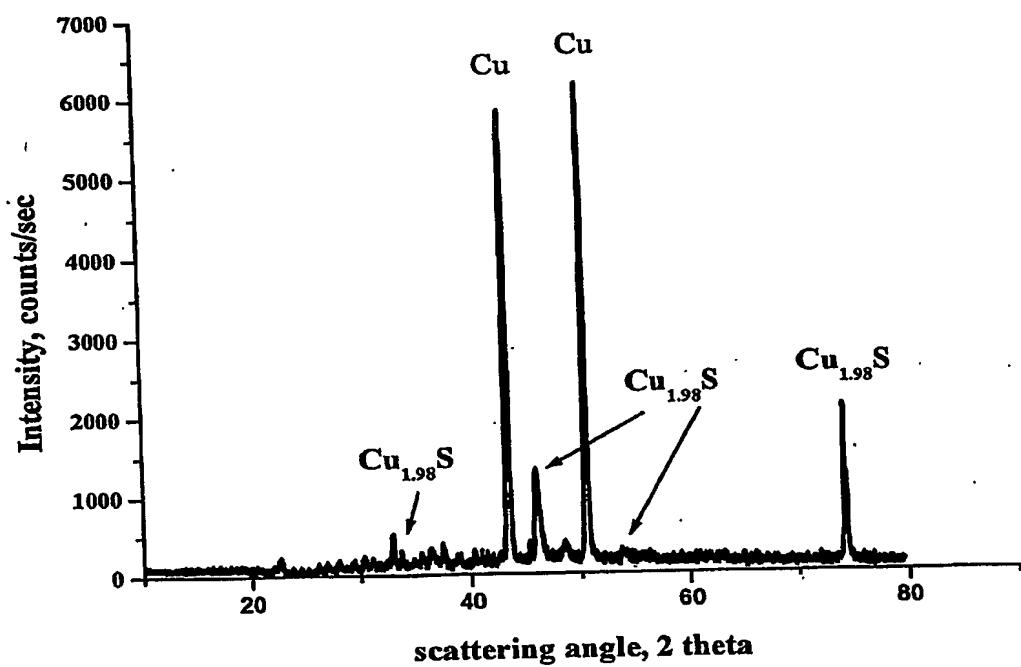


Fig. 4

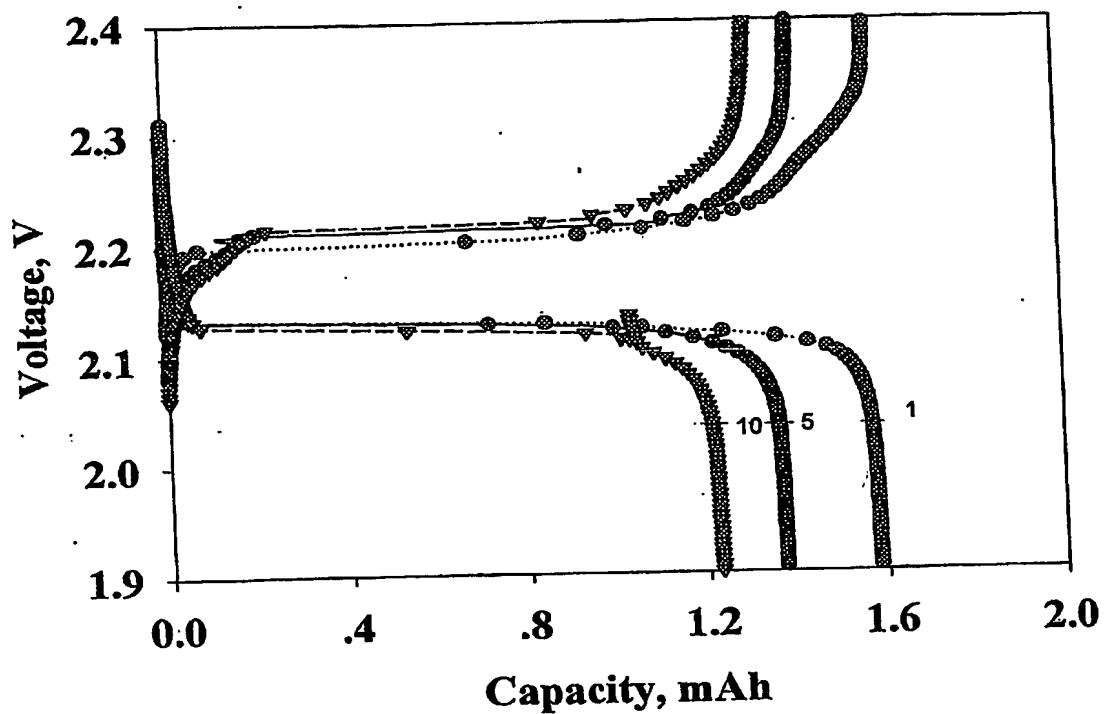


Fig. 5

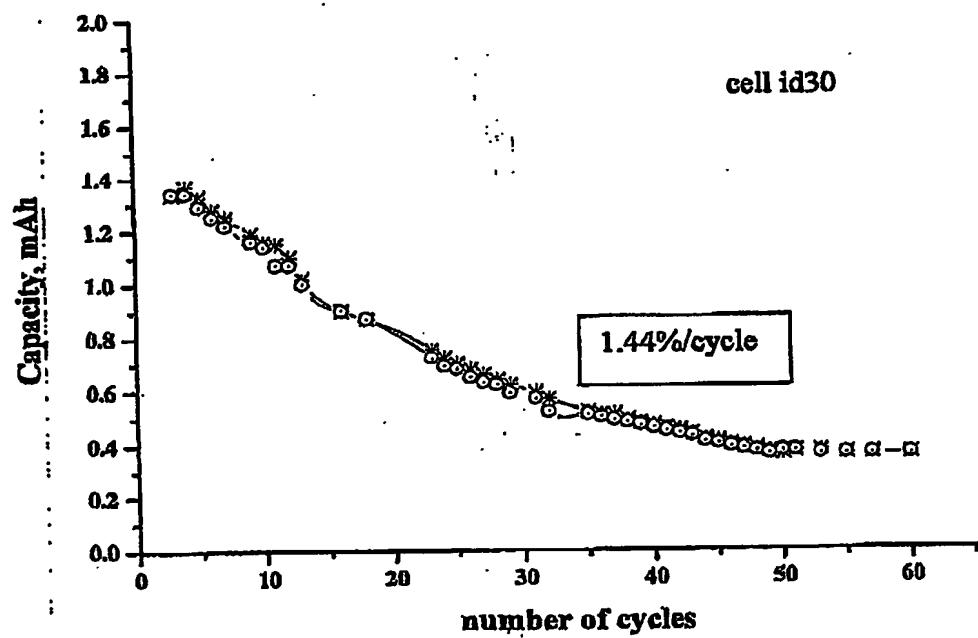


Fig.6

60416718 - 102702

Cathode  
active  
material

Ni layer

Silicon

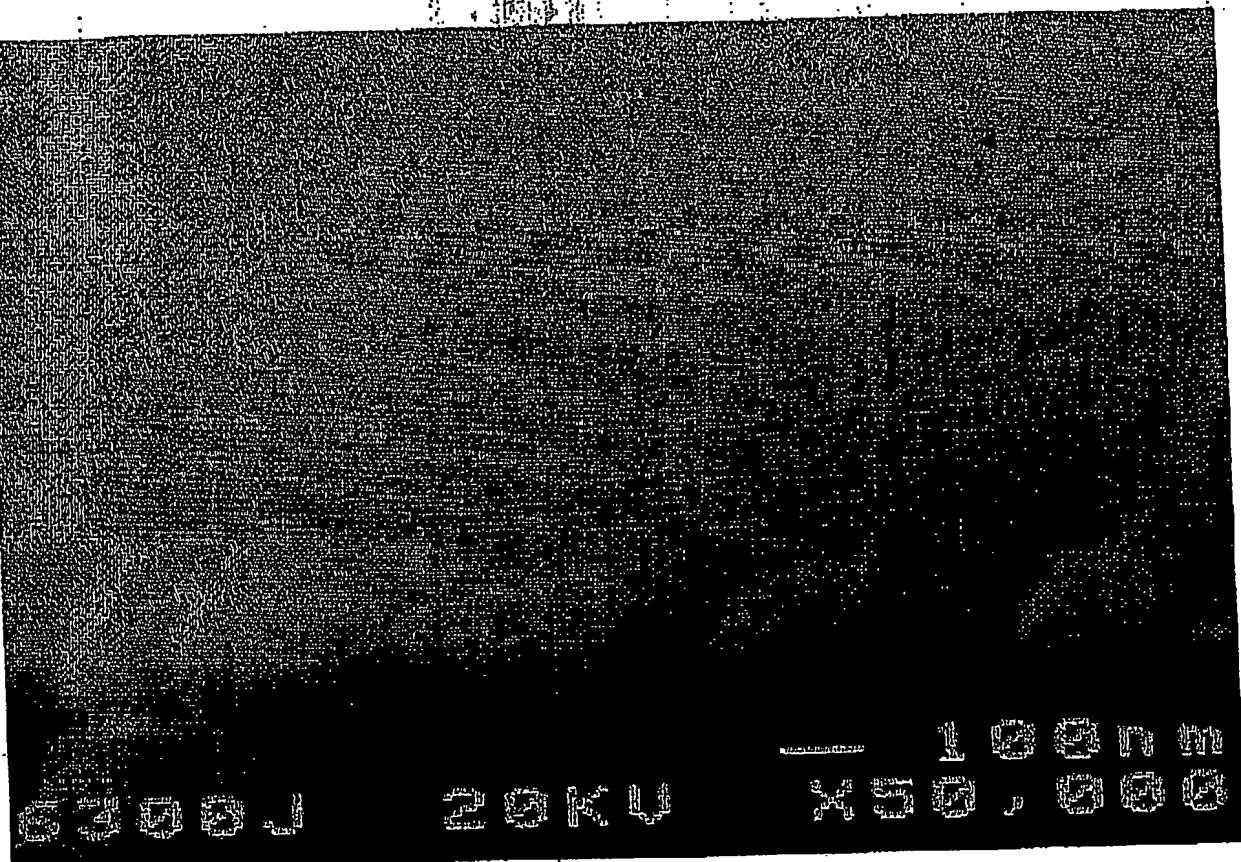


Fig.7

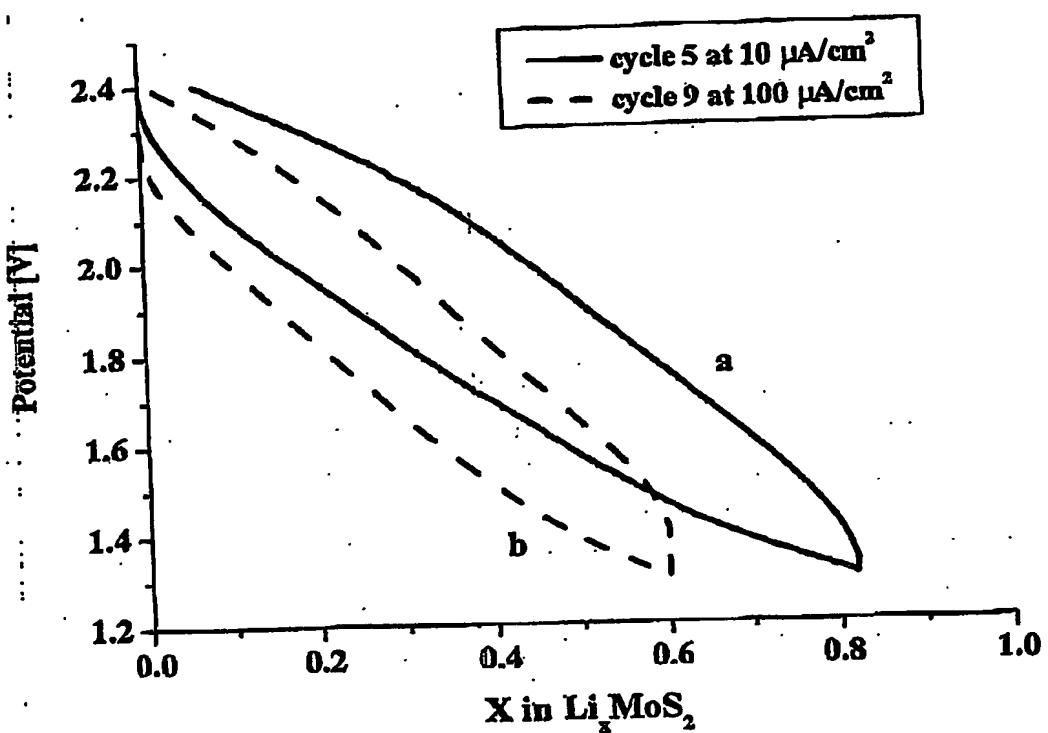


Fig. 8

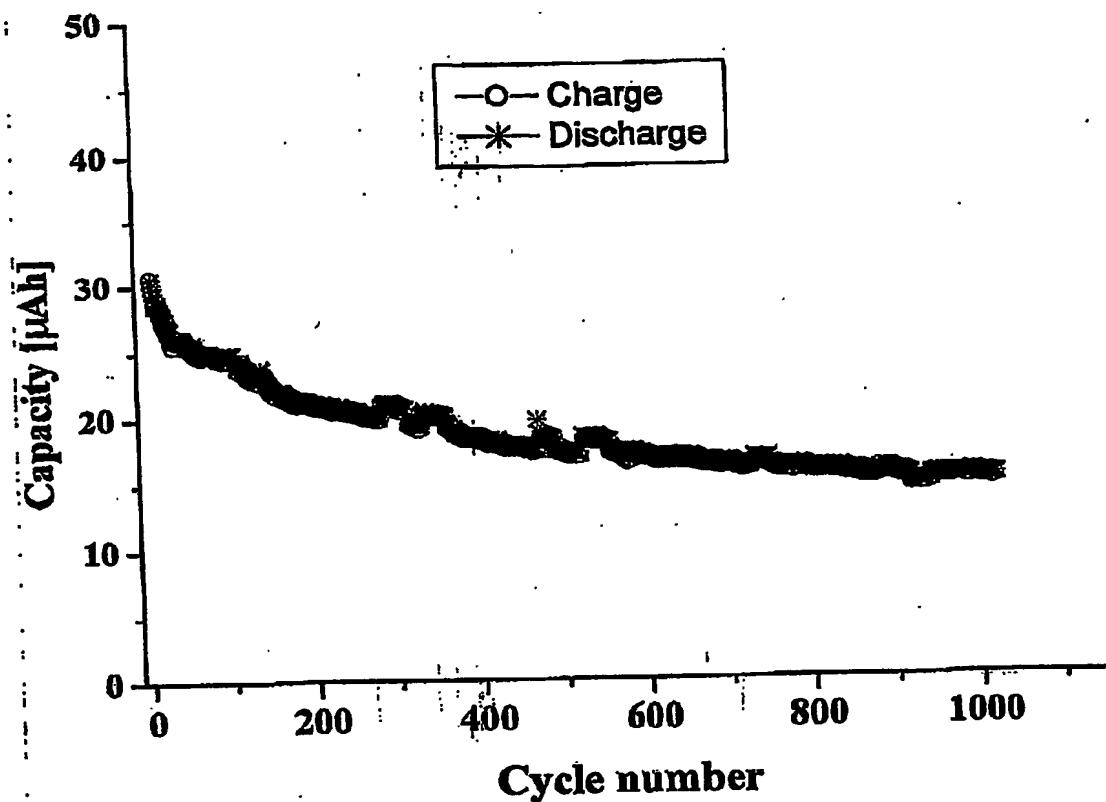


Fig. 9

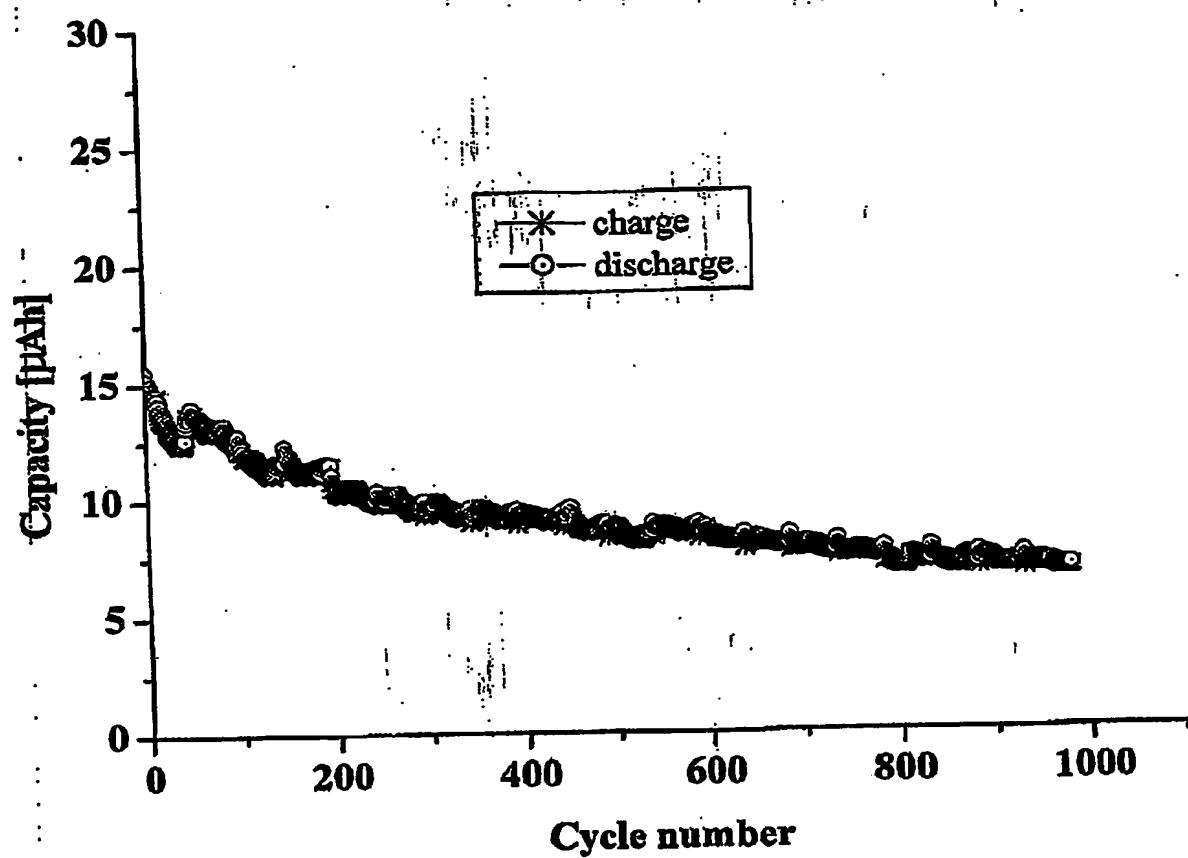


Fig.10

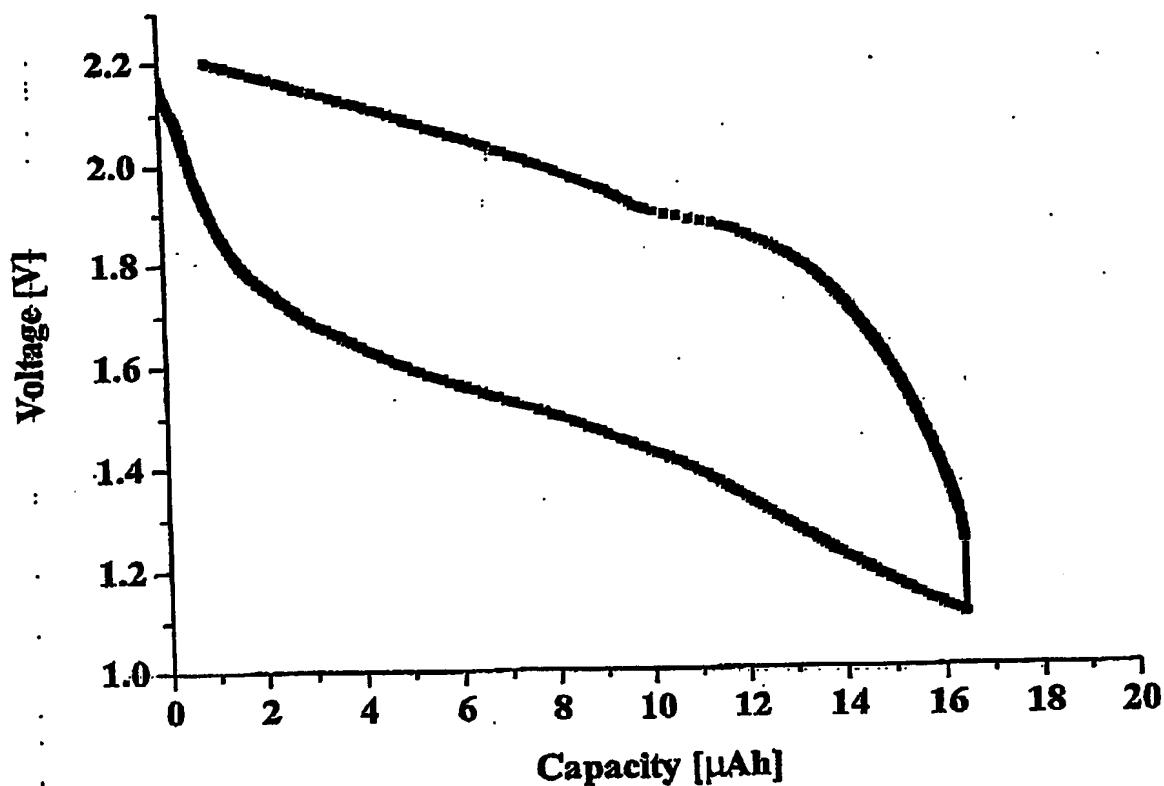


Fig. 11

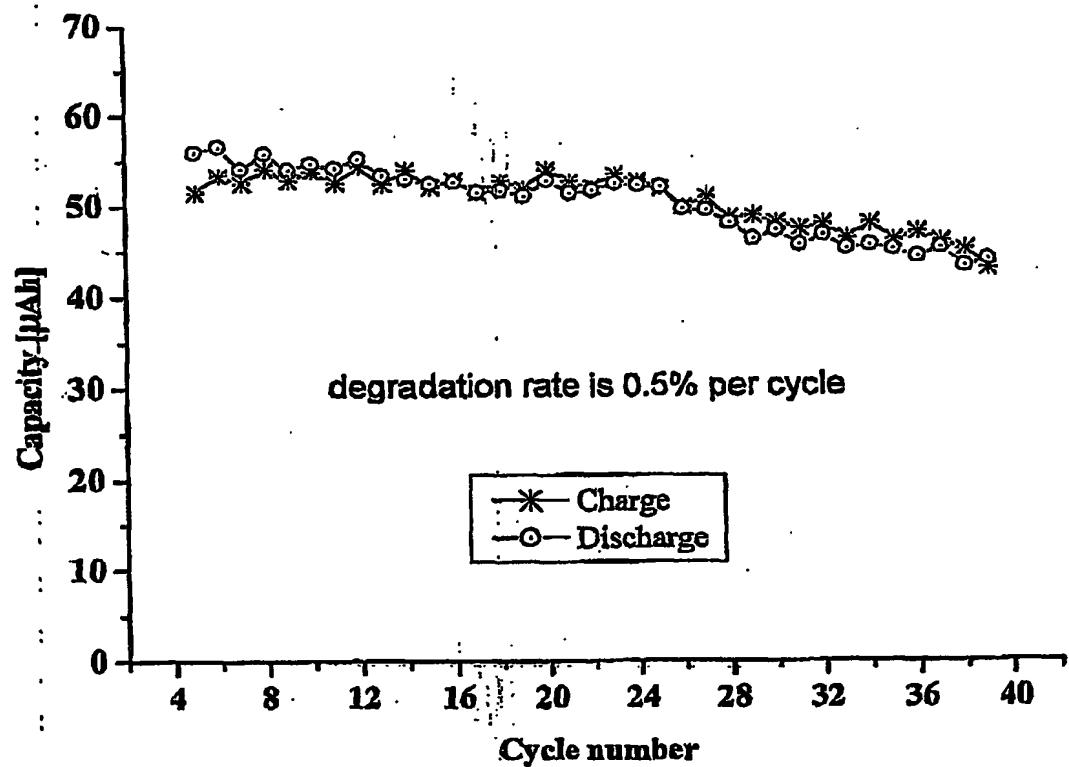


Fig.12

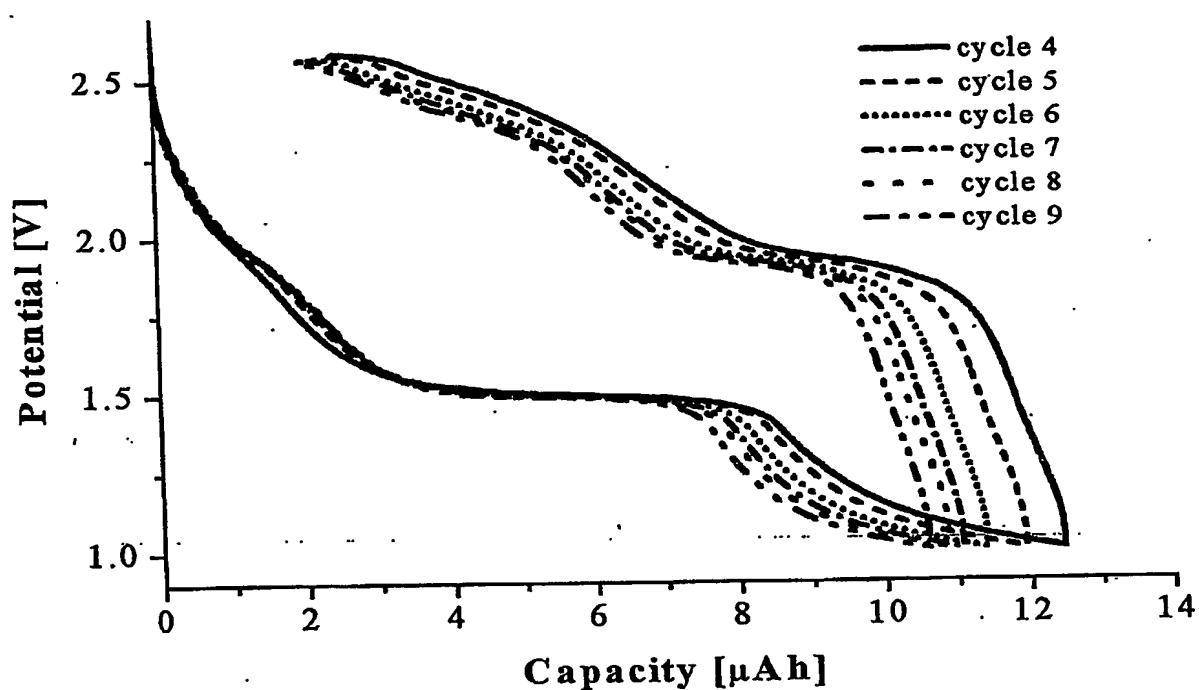


Fig. 13

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**